

A SELF-PERPETUATING CATALYST FOR THE PRODUCTION OF COMPLEX ORGANIC MOLECULES IN PROTOSTELLAR NEBULAE

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ABSTRACT

When hydrogen, nitrogen, and CO are exposed to amorphous iron silicate surfaces at temperatures between 500 and 900 K a carbonaceous coating forms via Fischer-Tropsch-type reactions. Under normal circumstances such a coating would impede or stop further reaction. However, we find that this coating is a better catalyst than the amorphous iron silicates that initiate these reactions. Formation of a self-perpetuating catalytic coating on grain surfaces could explain the rich deposits of macromolecular carbon found in primitive meteorites and would imply that protostellar nebulae should be rich in organic material.

Subject headings: astrobiology — astrochemistry — methods: laboratory — molecular processes — solar system: formation — stars: pre-main-sequence

Online material: color figure

1. INTRODUCTION

The formation of abundant carbonaceous material in meteorites is a long-standing problem (Hayatsu & Anders 1981) and an important factor in the debate on the potential for the origin of life in other stellar systems (Hornbeck 1995). Large quantities of complex prebiotic materials could greatly simplify chemical evolution in planetary environments starting from a rich organic broth and leading to the simplest forms of living organisms. Many mechanisms may contribute to the total organic content in protostellar nebulae, ranging from organics formed via ion-molecule and atom-molecule reactions in the cold dark clouds from which such nebulae collapse (Nuth et al. 2006), to similar ion-molecule and atom-molecule reactions in the dark regions of the nebula far from the protostar (Ciesla & Charnley 2006), to gas-phase reactions in subnebulae around growing giant planets (Fegley 1993) and in the nebulae themselves. It is unclear that any of these mechanisms could produce enough material to account for the relatively large quantities of organics found in the most primitive meteorites (Pizzarello et al. 2006).

The Fischer-Tropsch-type (FTT) catalytic reduction of CO by hydrogen to produce methane and other hydrocarbons was once the preferred model for production of organic materials in the primitive solar nebula (Hayatsu & Anders 1981; Pearce et al. 1989; Hindermann et al. 1993). The Haber-Bosch (HB) catalytic reduction of N₂ by hydrogen to make ammonia was thought to produce the reduced nitrogen found in meteorites. Both FTT and HB-type reactions have a major Achilles' heel when operating in the "dirty" environment around a protostar: the clean iron metal surfaces that catalyze these reactions are easily poisoned via reaction with any number of molecules, including the very same complex organics that they produce (Kress & Tielens 2001). In addition, both FTT and HB-type reactions work much more efficiently in the hot innermost regions of the nebula rather than in the cooler, lower pressure

environments where the asteroids—parent bodies for most meteorites—may have formed. Both of these problems may now be moot.

We have demonstrated that many grain surfaces can catalyze both FTT and HB-type reactions, including amorphous iron and magnesium silicates, pure silica smokes, and several minerals (Hill & Nuth 2003). Although none of these materials work as well as pure iron grains, and all produce a wide range of organic products rather than just pure methane, these materials are not truly catalysts. The properties of these surfaces change during the course of reaction and become more efficient as the reaction proceeds to build up a macromolecular grain coating that would usually serve to shut down such activity (Johnson et al. 2007). Indeed, amorphous iron silicate smokes that had accumulated a coating comprising 10% by mass carbon and 0.2% by mass nitrogen based on the total mass of the sample (Gilmour et al. 2002) remained an active and very efficient surface for production of nitrogen-bearing organic materials from a mixture of CO, N₂, and H₂. More recent work may provide a simple explanation for these observations: the carbonaceous grain coating is itself an efficient surface for the reduction of CO and N₂ by hydrogen to form a variety of organic materials.

2. EXPERIMENTAL DESCRIPTION

Llorca & Casanova (2000) demonstrated that FTT reactions occur under low pressures typical of the primitive solar nebula. Our experiments were designed to test the relative efficiency of various potential catalytic materials and to produce mixtures of solids and organics that could serve as analogs of primitive asteroidal material for later experiments. Grains in protostellar nebulae are exposed to the ambient gas for hundreds or even tens of thousands of years at pressures ranging from 10⁻³ to 10⁻⁴ atm or less. We do not have such times available for laboratory experiments, although we can duplicate the total number of collisions a grain might experience with components of the ambient gas by running experiments for shorter times at higher pressures. In our laboratory, experiments last from about 3 days at temperatures of 873 K to more than a month at temperatures of 573 K. If an average experiment lasts a week (6.05 × 10⁵ s), and if the only consideration for simulating the effects of the reaction is the total number of collisions of

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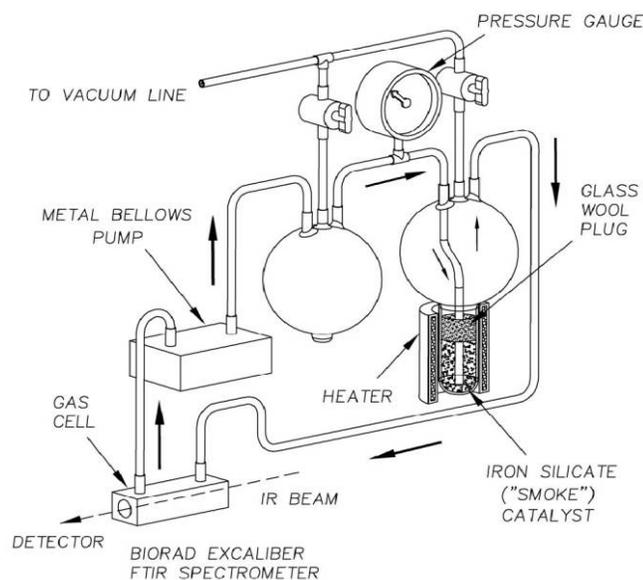


FIG. 1.—Simple experimental apparatus used to circulate reactive gas mixtures over potential catalysts at controlled temperatures and monitor the changes in the circulating gas via infrared spectroscopy.

potential reactants with the catalytic surface, then we can simulate two centuries (6.3×10^9 s) of exposure to an ambient gas at 10^{-4} atm by running experiments at ~ 1 atm total pressure. This scaling assumes that the reactants strongly bind to the surface of the catalyst and that this is the rate-controlling step. While it is true that the CO and N_2 must be strongly bound in order to weaken their bonds and thus increase their rates of reaction with H_2 , we are not certain that this is the rate-controlling step, although Kress & Tielens (2001) deduced that it must be. If the rate-controlling step is the reaction of H_2 with the CO or N_2 bound on the grain surface, then the important consideration is now the number of collisions of H_2 with the CO or N_2 bound on the catalyst rather than the number of collisions of CO or N_2 with the catalyst, and reaction time can once again be scaled to the number of collisions.

The situation becomes even more complicated if the CO and H_2 must “meet” at an active site on the catalyst surface. This scenario would be more like reactions that occur in the gas phase: the number of reactive collisions would therefore scale as the square of the total gas pressure. In our opinion, this is a worst case scenario as long as the reactants interact strongly with the catalytic surface. However, if true, then the week-long experiments discussed above would be the equivalent of 2 million years of nebular exposure rather than the 2 hundred years that we propose. In addition, doing experiments at pressures near 1 atm could conceivably affect the products synthesized in our experiments. We believe that the effects of temperature are much more important, but to avoid any minor effects due to changes in total pressure or due to changes in the relative partial pressures of the reactants we ran all of the experiments reported below with the same gas mixture and the same starting pressure: 75 torr CO, 75 torr N_2 , and 550 torr H_2 (700 torr initial pressure).

The experiments themselves were also very simple; see Figure 1 (Hill & Nuth 2003). We first load ~ 25 cm³ of catalyst into a glass finger through which gas can circulate by means of a glass tube that extends to the bottom of the finger. The finger is heated via an external mantle to a controlled temper-

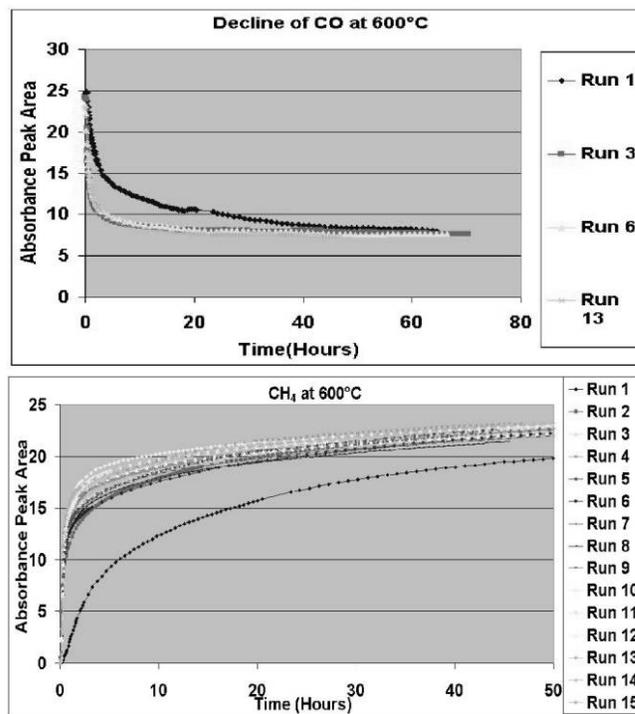


FIG. 2.—*Top*: Changing abundances of CO as a function of time in four separate runs using the same catalyst. *Bottom*: Changing abundances of methane in successive experimental runs at 873 K using the same catalyst. [See the electronic edition of the *Journal* for a color version of this figure.]

ature. We evacuate the system to a pressure of less than ~ 0.1 torr, then fill the system with gas (75 torr CO, 75 torr N_2 , 550 torr H_2) to a total pressure of 700 torr. We now begin to circulate gas using a bellows pump, begin heating the finger containing the catalyst, and record our first infrared spectrum of the gas (only CO is detected in this spectrum) using an FTIR spectrometer. The gas fluidizes the catalyst. The finger is plugged at the top of the heater using glass wool to contain the grains while letting the gas circulate. Some catalyst does get caught in the unheated glass wool for indefinite periods and some falls back into the glass finger. As the experiment proceeds we monitor progress by using periodic FTIR spectra to follow the loss of CO and the formation of methane, water, and carbon dioxide. We also monitor smaller spectral features due to ammonia and *N*-methyl methylene imine. Once the CO has been reduced to about 10% of its starting concentration we take a final infrared spectrum, turn off the heater, cool the system to room temperature, evacuate it to less than ~ 0.1 torr, then refill the system with fresh gas and begin a second run. Note that we do not use a fresh batch of catalyst for this second run as we want to follow the changing properties of the catalyst as a function of exposure to the gas mixture and as a function of temperature. By making ~ 15 runs with the same catalyst, we simulate ~ 3000 years of exposure of grains to nebular gas and build up a substantial coating of macromolecular carbon, nitrogen, and hydrogen.

3. RESULTS

Figure 2 (*top*) shows loss of CO with time for runs at ~ 873 K. The CO decays more slowly in the first run than in subsequent runs. The generation of methane as a function of time and run number is shown in Figure 2 (*bottom*); again, the rate is slower in the first run, but gets faster for subsequent runs. All gas-

phase products, with the exception of CO₂, follow the pattern set in Figure 2 (*bottom*) by methane in experiments carried out at 573, 773, and 873 K. CO₂ peaks, then decreases (depending on temperature), as the CO abundance declines below ~25%–30% of its initial level. At low levels of CO, the CO₂ is converted back into CO on the grain surfaces, slowing the apparent decay of CO, as is observed. All of our experimental runs followed this same pattern, with a much slower rate of change at lower temperatures, but a general increase in reaction rate after the catalyst was first exposed to the reactive gas. With more efficient catalysts and higher temperature experiments, the system quickly achieves the final “steady state” reaction rate.

For a typical, textbook catalyst, this result is counterintuitive. With each additional run, the catalyst forms slightly larger clumps, thus reducing surface area; the active metal atoms at the surface become more oxidized due to reaction with water generated by the FTT reaction; some reactive sites on the catalyst become coated by the macromolecular carbon generated in previous runs; and some catalyst simply gets trapped in the glass wool and is lost to the system. Each of these factors should slow reaction rates in subsequent experimental runs, yet we observe an increased rate of reaction after the first few runs, followed by a steady rate thereafter. One explanation for all of these observations, including the large mass fraction of carbon and nitrogen deposited onto the grains after ~20 runs, is that the macromolecular carbonaceous coating is a better FTT catalyst than the inorganic sites it covers. This hypothesis has several interesting consequences for FTT reactions in protostellar nebulae.

4. DISCUSSION

If the macromolecular coating itself promotes FTT and HB-type reactions, then there is no barrier to the deposition of a thick, multilayer organic coating on any grain surface. With traditional catalysts, no more than a monolayer can be deposited on a grain surface before the reaction stops; however, if the coating itself is a catalyst then one layer promotes the formation of the next, ad infinitum. If the macromolecular coating forms on any grain surface, even at very different rates, then all grain surfaces will eventually be coated and large quantities of CO (H₂ and N₂) will be fixed onto grain surfaces as a macromolecular organic coating. We note that it is much easier to incorporate such carbonaceous coatings into asteroidal parent bodies than it is to trap the more volatile products of traditional FTT or HB-type reactions such as methane or ammonia into these same bodies, since FTT and HB processes proceed more rapidly at higher temperatures and pressures, e.g., in the innermost regions of protostellar nebulae where layers of organic material could be quickly deposited onto grain surfaces.

We do not know why the carbonaceous grain coating is a better catalyst than the inorganic sites it covers. Metals within the silicates might remove electron density from the CO or N₂ triple bonds, thus weakening the bond and increasing rates of reaction with the ambient hydrogen. If the carbonaceous coating formed on the grains contains numerous aromatic subcomponents, then it is possible that these aromatic regions can also reduce the electron density in molecules that attach to the carbon network. If the network is always a “work in progress,” there should be numerous free radical sites on the coating’s surface which could bind ambient CO and N₂ molecules into the aromatic coating. Once bound into the growing macromolecular coating, the CO and N₂ molecules could more readily

react with adsorbed hydrogen due to their weakened bonds. Because there would be no limit to the growth of the coating, it could become much larger than the original inorganic catalytic site that first became coated, and thus might be a better catalyst only due to its much larger surface area. Alternatively, the free radical sites on the coating could more strongly bond to the ambient CO and N₂, the aromatic network could more efficiently weaken the bonds of the attached molecules, or both mechanisms could contribute to the increased catalytic efficiency. More experiments are necessary to sort out these possibilities.

While we assume that our experiments represent several hundred years of exposure to the nebular gas, it is possible that much longer exposures would be required in order to produce the relatively thick coatings observed in these experiments (10% C, 0.2% N by total mass) if the natural reactions are not pseudo-first order and the reaction rate is not linearly dependent on pressure. However, even if our estimates of the natural exposure time are incorrect, the observations that imply that the macromolecular carbonaceous coating is a better catalyst than the inorganic sites that it covers are still valid. Similar experiments carried out as a function of temperature are needed to resolve the scaling of time with the total number of collisions and to search for possible changes in the carbonaceous coatings produced in these reactions.

Although we previously suggested that transport must occur (Nuth 1999; Nuth et al. 2001; Hill et al. 2001) to bring thermally annealed, crystalline grains from the innermost nebula out to regions (100–200 AU) where comets form (Weidenschilling 1997), this hypothesis was spectacularly confirmed by the *Stardust* mission to comet Wild 2 (Zolensky et al. 2006). Grains from this comet, which should never have been inside the orbit of Jupiter during its formative stages, contain fragments of calcium aluminum inclusions (CAIs) and chondrules that could only form at the very high temperatures in the innermost regions of the solar nebula. If comet Wild 2 was never inside the orbit of Jupiter as it formed, then such materials must have been transported out to the growing comet. The combination of a self-perpetuating catalyst that forms naturally on any grain surface, together with widespread outward transport of materials formed in the hot, dense inner regions of protostellar nebulae, makes these nebulae gigantic organic chemical factories that turn abundant CO, N₂ and H₂ into complex hydrocarbons and seed organic material throughout the nebula. If circumstances that favor the chemical evolution of simple organisms can occur in planetesimals formed from such materials, then primitive organisms might take advantage of this natural bounty. While it is unclear that life will naturally evolve in such systems, it is abundantly clear that there will be copious quantities of organic material available to promote its chemical evolution.

5. SUMMARY

Laboratory experiments have demonstrated that a macromolecular, nitrogen-rich, organic coating forms on the surfaces of many different grain types and that this coating efficiently promotes the conversion of CO, N₂, and H₂ into additional layers of organic material. Such grain coatings could have been efficiently incorporated into growing planetesimals and would then be modified by heating, hydration, and other lithification processes that produced the modern population of asteroids and meteorites. Much more experimental work is required to understand the metamorphism of the initial organic materials con-

tained within various types of evolving planetesimal, and the analogs produced in these experiments are intended for such experiments. However, finding an organic coating that will naturally form under conditions in protostellar nebulae, and that will continue to grow as long as it is exposed to a CO, N₂, and H₂ rich gas at moderately high temperatures, adds an entirely new dimension to the chemistry of these nebulae. The organic content of protostars can no longer be modeled as the

remnant organic coatings on grains from parent dark molecular clouds, even with the addition of new materials formed by similar processes in the cold dark interiors of such nebulae. One must now account for abundant organic material produced in the innermost regions of these nebulae and transported outward, possibly to the Kuiper Belt and beyond, by the same mechanisms that brought crystalline grains and fragments of chondrules and CAIs to comet Wild 2.

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